Investigation of chemical composition of atmospheric aerosol in Siberian towns. Part 2. Microscale and seasonal variability of surface aerosol in Novosibirsk

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This work continues a cycle of our investigations in the framework of interdisciplinary project of SB RAS "Ecological Problems of Siberian Cities." In this part we consider seasonal dynamics of aerosol chemical composition in Novosibirsk city. Peculiarities in the aerosol formation in the city both at the cost of natural and anthropogenic sources are described.

The first part of our investigation[1] was devoted to description of experimental methods and means for studying the ecology of industrial cities of Siberia. We described synoptic conditions of the experiment, general dynamics of inorganic component in surface aerosol in the cities of Eastern Siberia; and the results of both of ion-element (up to 22 elements, 8 ions) and microcomponent (14 priority polyaromatic hydrocarbons) chemical composition of particles were considered in detail for three cities of the Irkutsk–Cheremkhovskii industrial region. In this paper, the emphasis is made on the seasonal aerosol variability in one city – Novosibirsk.

Conditions of the experiment

The aerosol sampling with the goal of subsequent analysis of aerosol chemical composition was performed during the mobile station movement and at its stops at day time on March 19 and July 30, 2004, in Novosibirsk. Figure 1 shows a continuous variation of the carbon monoxide concentration during the first day of sampling, started at 9:50 LT at the northern point of the route near the city airport "Severnyi" and ended at 15:50 LT at the southern point of Akademgorodok.

The peaks of the CO concentrations correspond to the mobile station routes between points of aerosol sampling, numbered in Fig. 2 from 1 to 5. Three first passages of the mobile station went along city ways with a heavy traffic; the last portion of the route refers to the well wind-blown roundabout road between the city and Akademgorodok. Points of aerosol sampling were chosen at a maximally possible distances from motorways. Nevertheless, it is evident that, for instance, during aerosol sampling on 19 March made from 15:10 LT to 15:50 LT near the Institute of Computational Mathematics and Mathematical Geophysics in Akademgorodok we failed to eliminate or effectively decrease the transport effect.

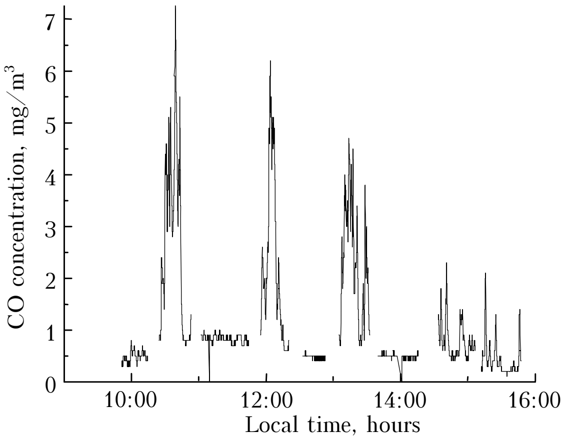

Fig. 1. Spatiotemporal profile of the carbon monoxide concentration during measurements on 19 March, 2004.

The synoptic conditions during the experiment were the following.

On March 19, 2004, the weather in Novosibirsk was determined by the north periphery of the Asian anticyclone centered in the vicinity of Kyzyl. During daytime the anticyclone weakened, changed its configuration and locations of high-pressure nuclei at its central part. The temperature – humidity regime of the region under study was determined by the continental temperate air mass.

On July 30, 2004, the weather was determined by the contrast zone between the cyclone in the south of the Omsk Region and the anticyclone centered over the Kola Peninsula. The air mass during measurements was the old continental arctic mass. In both cases in the fundamental flow the western transfer predominated.

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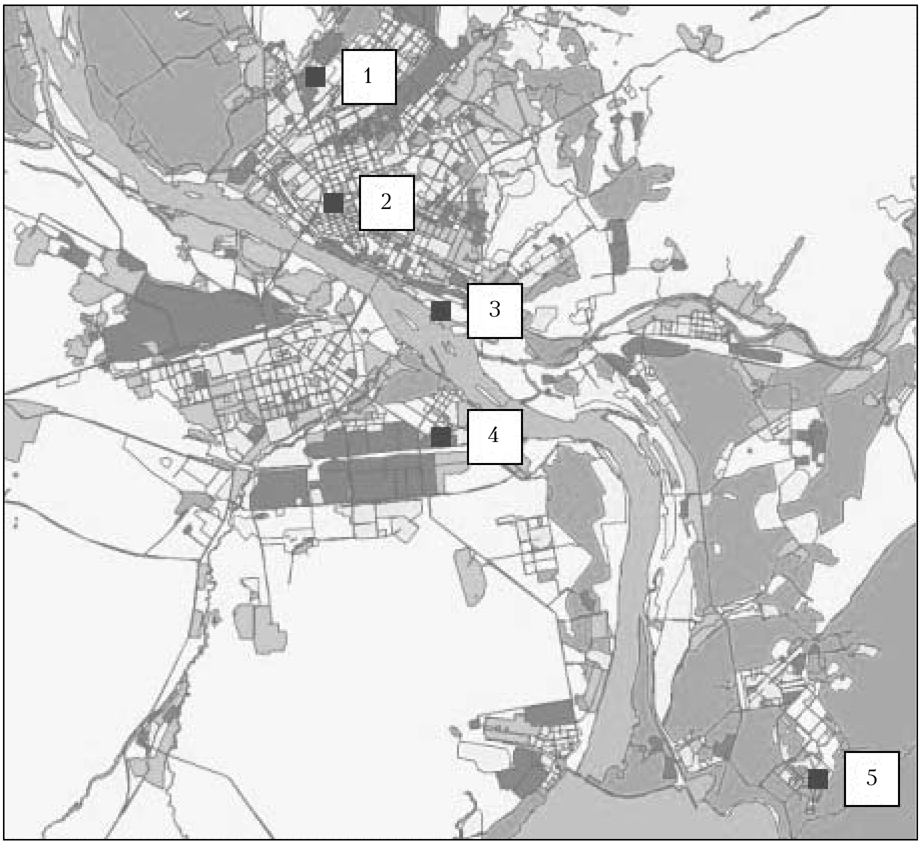

Fig. 2. Diagram of location of sampling points at the mobile station stops on 19 March and 30 July 2004.

Discussion of results

Referring to measurement conditions taking place during the series of experiments with the spatio-temporal profile of carbon monoxide concentration as an example, is not accidental. It is well known that CO is one of the first indicators of intensity of motor transport emissions. The city of Novosibirsk due to its position is the greatest transport center beyond the Ural. Based on the latest statistical data,[2] the Novosibirsk region heads the list of regions and territories of the Siberian Federal district by the percentage of pollutant emissions into atmosphere from movable sources. In 2003, about 31% of atmospheric emissions in the region referred to stationary sources.

The situation in the regional center was much more crucial. Gross emission of pollutants from stationary sources in 2003 was 100000 tons, and from the movable sources – 459.4 thousand tons, i.e., more than 80% of all emissions in atmosphere fell on the transport with the most adverse impact on the nature and urban medium performed by the motor transport. Besides, the main sources of pollution of the atmospheric air in Novosibirsk are also the enterprises of power industry, municipal boiler-rooms (housing department), the stove heating in the private sector, the electrode plant.

Table 1 shows some measured atmospheric parameters attendant the aerosol sampling. In the next to last line, the measurements of the aerosol number concentration NS in the size range $0.4 \le d \le 10$ μm obtained with a photoelectric counter AZ-6 are given. The last line contains the data on the total concentration of the measured ions and elements.

Disposition of sampling points in the city is almost meridional (Fig. 2). The first and the last points are located, in fact, in the city suburbs. The net concentrations both of the particle number density, NS, and the ion-element sum (Sum) show that the tendency of accumulation of aerosol pollutions in the central part of the city is clearly seen during the cold period. In summer, the pattern is somewhat dissimilar and not distinct: the number density follows with a certain redistribution the winter values, but the correlation of the sum of ions and elements with them is less significant.

In this connection, a special attention must be given to distribution of field of the surface wind velocity V in both seasons, which was measured at sampling points at a 10 m height, using a telescope mast. On March 19, we observed almost complete absence of wind at the outskirts – 1–2 m/s and an increase of the surface wind velocity up to 9–10 m/s to the city center. Therewithal, a turn of wind direction wd up to 140° was recorded in the center as compared to the outskirts. In a summer day, the wind turn is insignificant and does not exceed several tens of degrees that can be attributed to the effect of urban building. As for the wind velocity, the pattern is almost opposite to the winter one: a weak wind in the central part of the city and a growth of the ground flow velocity to the periphery.

To elucidate the nature of aerosol pollution in different parts of the city in different periods, let us consider the relative chemical composition (Fig. 3) and geochemical enrichment coefficients of aerosol components (Table 2).

Consideration of relative aerosol composition from the point of view of microscale variability shows some increase of relative content of sulfate component and microelement composition in the outskirts direction, especially in winter period. Seasonal dynamics of relative composition is more significant. The content of macrocomponents: aluminium, calcium, and silicon commonly attributed to the soil-erosion origin, is invariable. The iron content, which is also considered as a soil reference point, actually increases in summer by more than the order of magnitude that supports its predominantly natural origin. Just this fact enabled us to take it as a reference element when estimating the origin of other components in the city aerosol composition.

The sulfate content in summer period slightly decreases (Fig. 3). At the same time, the concentrations of nitrogen-containing components increases significantly. This strongly discriminates the behavior of the city aerosol from the background one.

As was shown by results of long-term investigations of surface atmospheric aerosol ion composition in the background points of the Novosibirsk Region,[3] the dynamics of acid-forming ions: sulfate, nitrate, and neutralizing them cations of ammonium has a seasonal winter maximum. In our case, this was only partly true for the sulfate component, and the maxima of nitrate and ammonium fell on the summer period. Possibly, this is connected with active all-seasonal generation of gases-predecessors of the nitrogen component under city conditions (Table 1). For active formation of photochemical component of aerosol, a presence of photochemical processes is required, which in winter period are retarded in cities not only by a seasonal minimum of the incident solar radiation, but also by ultraviolet radiation absorption by the pollution “cap” in the atmospheric boundary layer above the city. It is also possible that the sink of nitrogen-containing gas-predecessors on the snow cover increases in winter.

Consideration of geochemical enrichment coefficients indicates that the anthropogenic contribution to aerosol in winter period is dominant practically for all elements, with rare exception: probably, iron itself, potassium, and partly magnesium. It is evident, that the majority of elements in aerosol in winter are of ash origin from emissions of coal-consuming power plants. In the summer aerosol, the enrichment of practically all elements corresponds to the conventionally natural standard (< 1) or is close to it (< 10). The ion composition behaves more ambiguously, and in this case the demarcation in its behavior again goes between the nitrogen-containing ions, whose enrichment is invariable from one season to another, and other anions, whose relative content in relation to iron in summer reduces by one or two orders of magnitude. It is unlikely that such almost direct dependence of contents of iron, ions of ammonium, and nitrates in the urban aerosol composition is regular, although it should not be rejected completely.

Table 1. Parameters of the ground atmosphere measured at five points of Novosibirsk from the mobile station of air monitoring AKV-2

Parameter	March 19, 2004					July 30, 2004				
	Airport ”Severnyi”	CPC	River port	Area of tin plant	Akadem-gorodok	Airport ”Severnyi”	CPC	River port	Area of tin plant	Akadem-gorodok
t, °C	–6.44	–8.34	–6.37	–5.35	–10.04	23.48	22.77	24.63	23.91	19.29
rH, %	64.00	74.03	62.50	58.54	74.21	40.46	40.81	36.65	38.06	48.73
P, mm Hg	751.14	758.66	763.92	761.29	758.06	744.17	744.09	748.35	747.05	741.91
Q, W/m^2	–	–	568.39	490.32	168.35	210.52	43.04	675.93	699.64	658.97
V, m/s	1.00	1.52	9.33	5.12	1.95	5.14	2.12	2.72	1.33	4.87
wd, deg.	137.6	277.5	210.7	234.0	134.4	64.1	55.9	62.5	79. 8	63.9
CO, mg/m^3	0.22	0.84	0.48	0.49	0.47	0.40	0.56	0.84	0.30	0.36
O_3, μg/m^3	82.34	31.36	93.35	87.21	71.46	47.48	35.37	33.45	48.40	40.10
SO_2, μg/m^3	57.54	118.58	16.26	24.63	46.58	0.94	3.98	3.09	0.00	0.57
NO_2, μg/m^3	29.62	53.52	12.17	18.54	26.58	10.59	19.28	30.26	5.72	14.06
NO, μg/m^3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.83	0.0	0.73
NS, cm^{-3}	1.56	3.88	2.37	2.04	0.75	1.68	1.79	2.94	2.62	2.11
Sum, μg/m^3	53.1	159.8	66.0	74.8	57.3	56.0	34.3	57.3	34.3	66.9

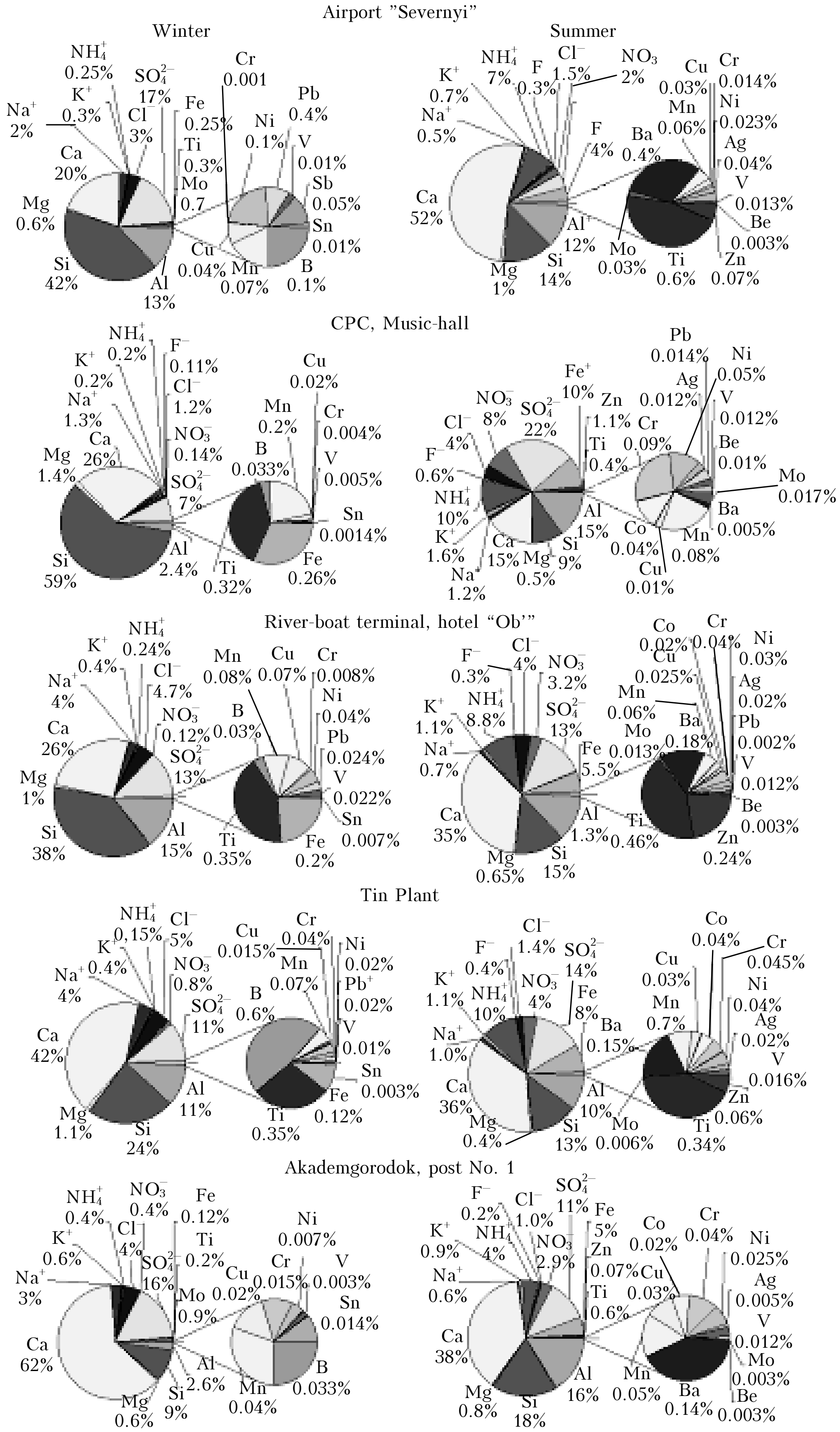

Fig. 3. Relative ion-element composition of surface aerosol at different periods of observations.

Table 2. Geochemical enrichment coefficients for aerosol components (Fe as a reference element, the element and ion complexing agent abundances – by Beus)

Chemical element	March 19, 2004					July 30, 2004				
	Airport "Severnyi"	CPC	River port	Area of tin plant	Akademgorodok	Airport "Severnyi"	CPC	River port	Area of tin plant	Akademgorodok
Al	24.0	4.2	34.0	42.0	9.9	1.5	0.7	1.0	0.6	1.4
Si	23.0	30.0	26.0	26.0	10.0	0.5	0.1	0.3	0.2	0.4
Mg	7.4	16.0	8.9	28.0	14.0	0.7	0.2	0.4	0.2	0.5
Ca	$1.2 \cdot 10^2$	$1.5 \cdot 10^2$	$1.9 \cdot 10^2$	$5.0 \cdot 10^2$	$7.5 \cdot 10^2$	21.0	2.3	9.2	6.8	10.0
Na^+	15.0	8.1	18.0	55.0	39.0	0.2	0.2	0.2	0.2	0.2
K^+	1.6	0.9	2.1	4.4	6.7	0.3	0.2	0.3	0.2	0.2
NH_4^+	11.0	6.5	14.0	14.0	36.0	23.0	12.0	17.0	14.0	9.4
F^-	–	22.0	–	–	–	3.7	3.1	2.8	2.8	2.4
Cl^-	$2.8 \cdot 10^3$	$9.6 \cdot 10^2$	$5.2 \cdot 10^3$	$8.9 \cdot 10^3$	$7.2 \cdot 10^3$	91.0	90.0	$1.7 \cdot 10^2$	40.0	43.0
NO_3^-	–	1.6	2.0	21.0	10.0	1.7	2.4	1.8	1.8	1.7
SO_4^{2-}	$2.1 \cdot 10^3$	$7.8 \cdot 10^2$	$2.0 \cdot 10^3$	$2.6 \cdot 10^3$	$4.2 \cdot 10^3$	35.0	68.0	70.0	53.0	66.0
Mo	$8.0 \cdot 10^4$	–	–	–	$2.2 \cdot 10^5$	$2.2 \cdot 10^2$	47.0	64.0	21.0	14.0
Ti	12.0	14.0	19.0	31.0	18.0	1.7	0.4	0.9	0.5	1.3
Fe	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mn	16.0	36.0	21.0	28.0	17.0	0.8	0.4	0.6	0.5	0.5
Ni	$5.2 \cdot 10^2$	–	$3.0 \cdot 10^2$	$2.3 \cdot 10^2$	77.0	9.1	6.5	7.1	7.1	6.6
Cu	$2.5 \cdot 10^2$	$1.2 \cdot 10^2$	$6.1 \cdot 10^2$	$2.0 \cdot 10^2$	$2.7 \cdot 10^2$	12.0	1.9	7.3	6.5	11.0
Pb	$3.8 \cdot 10^2$	–	$2.8\ 10^2$	$3.8 \cdot 10^2$	–	1.1	3.3	1.0	0.8	0.6
V	24.0	8.5	53.0	43.0	13.0	1.8	0.6	1.0	0.9	1.1
Cr	5.4	18.0	43.0	$3.2 \cdot 10^2$	$1.4 \cdot 10^2$	4.3	10.0	7.3	6.2	7.2
Sn	$4.3 \cdot 10^2$	70.0	$5.0 \cdot 10^2$	$3.3 \cdot 10^2$	$1.6 \cdot 10^3$	–	–	–	–	–
B	$1.5 \cdot 10^3$	$4.6 \cdot 10^2$	$5.6 \cdot 10^2$	$1.7 \cdot 10^4$	$1.0 \cdot 10^3$	–	–	–	–	–
Sb	$3.7 \cdot 10^4$	–	–	–	–	–	–	–	–	–
Zn	–	–	–	–	–	15.0	79.0	31.0	5.1	10.0
Ba	–	–	–	–	–	5.6	$2.6 \cdot 10^{-2}$	1.7	1.0	1.4
Be	–	–	–	–	–	11.0	14.0	8.4	–	7.2
Co	–	–	–	–	–	–	22.0	18.0	26.0	21.0
Ag	–	–	–	–	–	$4.6 \cdot 10^3$	$4.9 \cdot 10^2$	$1.3 \cdot 10^3$	$9.3 \cdot 10^2$	$3.7 \cdot 10^2$

At least, the contribution of heterogeneous oxidation processes of sulfur dioxide on the surface of solid aerosols, containing oxides of transition metals, including aquacomplexes of iron ions, has already been recognized.[4] However, in accordance with the same reference, the key role in formation of nitric acid from nitric oxides belongs to homogeneous gas-phase reactions. The contribution of reactions in water phase or heterogeneous processes is considered to be insignificant.

In conclusion, one more table is given, which allows one to estimate the differences in chemical matrix of city aerosol in cold and warm seasons by the simple ratios method. In addition, the table contains ratios between standard deviations and mean values for every series of measurements. The components are presented in order of decreasing the winter-to-summer ratios.

A relatively even stable excess of ions of chloride, sodium, and sulfate component in the aerosol composition is observed during the cold period over the entire profile. This, most likely, is due to comparable power of their natural and industrial sources. Among chemical elements, contribution of silicon, manganese, and copper is predominant. Such irregular excesses are connected, evidently, with the point sources of their emissions in the composition of aerosol coarse-dispersion fraction (silicon, magnesium, manganese, calcium, titanium). Components located in the bottom of Table 3 are of soil-erosion or photochemical origin. The low seasonal ratio, typical for chromium, at a 4.7-fold total excess of aerosol net concentration against the background of sufficiently high geochemical ratio in summer (10.0) (Table 2), can point to the surface source of this microelement, probably, of anthropogenic origin near the measurement place.

According to Ref. 5, the magnitude of ratios of standard deviations to mean values in one measurement series can also serve as a criterion of degree of localization of the origin of some component in aerosol composition. Nevertheless, despite the fact that in some cases, especially in winter measurement series, our arguments often coincide with this conclusion, the problem of using these ratios as the criterion, remains as yet open. Probably, the choice of criterion for estimates of some ingredient contribution into the aerosol composition is the problem of a special study, which must base on much more representative material. In our case, these ratios are of interest as characteristics of microscale variability of aerosol components within the city boundaries.

Table 3. Ratios of absolute concentrations of aerosol chemical components during cold and warm periods (winter/summer), as well as standard deviations to the mean value

Chemical element	Airport "Severnyi"	CPC	River port	Area of tin plant	Akadem-gorodok	St.d./mean winter	St.d./mean summer
Mo	23.95	–	–	–	309.83	1.40	0.87
Pb	22.07	–	11.45	14.96	–	0.95	0.92
Na$^+$	4.55	4.84	3.56	8.90	3.96	0.38	0.19
Cl$^-$	2.03	1.33	1.26	7.62	3.27	0.34	0.67
SO$_4^{2-}$	3.91	1.42	1.13	1.68	1.24	0.13	0.40
Si	2.85	29.91	3.32	3.93	0.43	1.07	0.48
Mg	0.69	13.61	1.02	6.20	0.58	1.01	0.54
Mn	1.23	10.57	1.54	1.89	0.63	1.24	0.14
Cu	1.38	8.12	3.36	1.07	0.49	0.64	0.52
Ca	0.36	7.96	0.83	2.52	1.41	0.48	0.52
Ti	0.48	4.12	0.86	2.21	0.28	0.63	0.50
Ni	3.74	–	1.72	1.10	0.23	1.04	0.11
V	0.90	1.88	2.11	1.52	0.24	0.58	0.25
Al	1.02	0.75	1.32	2.45	0.14	0.55	0.41
Cr	0.08	0.22	0.24	1.76	0.37	1.05	0.45
F$^-$	–	0.86	–	–	–	–	0.15
K$^+$	0.41	0.50	0.33	0.76	0.56	0.30	0.22
NO$_3^-$	–	0.08	0.04	0.40	0.12	1.02	0.31
Fe	0.07	0.12	0.04	0.03	0.02	0.85	0.21
NH$_4^+$	0.03	0.07	0.03	0.03	0.07	0.34	0.21
Sum	0.95	4.66	1.15	2.18	0.86	0.54	0.30

Conclusion

The investigation of urban aerosol in the largest megapolis of Siberia demonstrated a high variability in distribution of aerosol and its individual components in the cold period due to the presence of supplementary high-power sources in winter and to a higher development of local urban circulation blocking the pollution inside the city territory. In summer period, most likely, this circulation has smaller horizontal dimensions, and impurities are capable of greater scattering in the vertical direction.

Acknowledgments

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